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DZIAŁ C

CHEMIA I METALURGIA

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(54) **Sposób redukcji ditlenku siarki do siarki elementarnej w strumieniu plazmy**

(57) Sposób redukcji ditlenku siarki do siarki elementarnej, przez reakcję ditlenku siarki z reduktorem w strumieniu plazmy, polega na tym, że ditlenek siarki wprowadza się do strefy reakcji poza strefą generacji strumienia plazmy, zaś reduktor stanowi składnik gazu plazmotwórczego lub reduktor wprowadza się do strefy reakcji obok ditlenku siarki.

(3 zastrzeżenia)

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(54) **Sposób i urządzenie do otrzymywania objętościowego monokrystalicznego azotku zawierającego gal**

(57) Sposób otrzymywania objętościowego monokrystalicznego azotku zawierającego gal odbywa się w autoklawie, w środowisku rozpuszczalnika nadkrytycznego zawierającego jony metali alkalicznych i polega na rozpuszczeniu materiału źródłowego i utworzeniu roztworu nadkrytycznego oraz jednoczesnej lub oddzielnej krystalizacji azotku zawierającego gal z tego roztworu na powierzchni zarodka w temperaturze wyższej i/lub ciśnieniu niższym niż dla procesu rozpuszczania. Sposób jest realizowany w urządzeniu do otrzymywania objętościowego monokrystalicznego azotku zawierającego gal, zaopatrzonym w autoklaw (1) do wytworzenia nadkrytycznego rozpuszczalnika, wyposażony w instalację (2) do ustalenia przepływu konwekcyjnego, osadzony wewnątrz pieca lub zespołu pieców (4), wyposażonego w urządzenia grzejne (5) i/lub urządzenia chłodzące (6).

(24 zastrzeżenia)
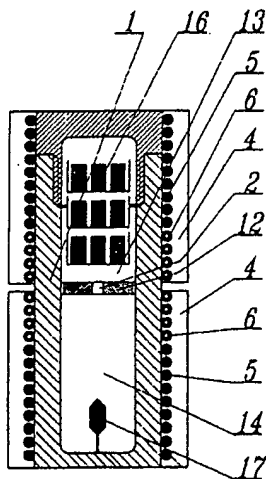
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(54) **Dezaktywacja skażeń naftowych z wykorzystaniem bakterii utylizujących alkany**

(57) Przedmiotem wynalazku jest sposób rozkładania naftowego czynnika skażającego, który to sposób obejmuje obrabianie skażenia naftowego bakteriami utylizującymi alkany w obecności co najmniej jednego alkanu i tlenu przez okres obróbki wystarczający dla bakterii utylizujących alkany do rozłożenia skażenia naftowego. Przedmiotem wynalazku jest też sposób odkażania wody i miejsca skażonego.

(43 zastrzeżenia)

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(54) **Osadnik żużla**

(57) Osadnik żużla posiada dwa równoległe ciągi, zawierające szeregowo połączone: komorę osadczą (1), komorę klarowania (2) i komorę wodną (3). Pomiędzy komorami klarowania (2) a komorami wodnymi (3) jest pompownia wody drenażowej (5) i jeden wspólny zbiornik wody drenażowej (4). Ściana tylna komory klarowania (2) jest zaopatrzona od góry w wylewy (6) z elementami odcinającymi (7). Wylewy (6) są umieszczone na różnych poziomach poniżej przelewu (8) i od strony komory klarowania (2) są chronione blachami żaluzjowymi (9). Dno komory osadczej (1) i dno komory klarowania (2) mają pochylenie rzędu 0,5 % w kierunku przepływu wody. Usytuowane na ich dnach złoża filtracyjne (1) posiadają poprzecznie ułożone dreny szczelinowe (11), zakończone u góry szyną, wyposażoną na każdym końcu w dwustronny uchwyt w kształcie grzybka. Każdy dren szczelinowy (11) posiada na ścianach bocznych poprzeczny wylew, którym łączy się z sąsiednim drenem szczelinowym (11), przy czym miejsce styku poprzecznych wylewów sąsiednich drenów szczelinowych (11) jest nakryte dopasowaną obejmą z kabłąkowym uchwytem.

Dren szczelinowy (11) posiada konstrukcję szkieletową, umocowaną do prostokątnej podstawy o bokach wielokrotnie większych od szerokości. Na końcu podstawy oraz w co najmniej pięciu miejscach, dzielących jej powierzchnię na jednakowe płaszczyzny, znajdują się prostopadłe płyty czołowe w kształcie prostokąta ze ściętymi górnymi rogami pod kątem co najmniej 50°. Wewnętrzne płyty czołowe posiadają od dołu, usytuowane osiowo, podłużne prostokątne wycięcie. Na ścianach bocznych każdego drenu szczelinowego (11), od podstawy do punktu ścięcia górnych rogów płyty czołowej jest prostokątna płyta boczna z otworem w kształcie zaokrąglonego u góry prostokąta. Do krawędzi otworu umocowany jest wylew, którego przekrój poprzeczny jest identyczny z kształtem otworu. Do ściętych górnych krawędzi płyt czołowych oraz do ich powierzchni czołowych są umocowane ukośnie, w jednakowych od siebie odległościach na całej ich wysokości, równoległe blachy tworzące żaluzjowe boki drenu szczelinowego (11) z kanałami filtracyjnymi w postaci skrzeli.

Dreny szczelinowe (11) złoża filtracyjnego (10) komory osadczej (1) i złoża filtracyjnego (10) komory klarowania (2) są

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Verified English translation from the Polish language

PATENT OFFICE OF THE REPUBLIC OF POLAND

[State emblem]

CERTIFICATE

AMMONO Sp. z o.o.

Warszawa, Poland

NICHIA CORPORATION

Tokushima-Ken, Japan

filed with the Patent Office of the Republic of Poland on 6th June, 2001 an application for granting a patent for the invention entitled:

"Process and apparatus for obtaining of bulk mono-crystalline gallium-containing nitride".

The description of the invention, the claims and drawings attached to this certificate are the true copies of the documents filed along with the application on 6th June 2001.

The application was filed under number P-347918.

Warsaw, 9th September 2002

under authorization of The President

[Pressed round seal with the emblem of the Republic of Poland and an illegible circumscription – put on a round piece of paper attached to the ribbon binding the 19 pages of the document.]

[illegible signature]

Jowita Mazur, M.A.
Officer in charge

Process and the apparatus for obtaining of bulk mono-crystalline gallium-containing nitride

The object of this invention is the process for obtaining of bulk monocrystalline

5   gallium-containing nitride through its crystallization from a supercritical solution on a seed, as well as the apparatus for obtaining bulk monocrystalline gallium-containing nitride, in particular the apparatus for the production of bulk monocrystalline gallium nitride by a process employing supercritical NH_3.

Optoelectronic devices based on nitrides are usually manufactured on sapphire or

10   silicon-carbide substrates that differ from the deposited nitride layers (so-called heteroepitaxy). In the most often used MOCVD method, the deposition of GaN is performed from ammonia and metal-organic compounds in a gas phase, while the growth rates reached make it impossible to afford a bulk layer. The application of a buffer layer reduces the dislocation density, but not more than to approx. $10^8/cm^2$. Another method was

15   proposed for obtaining of bulk monocrystalline gallium nitride. It consists in an epitaxial deposition employing halides in a vapor phase (HVPE) [„Optical patterning of GaN films" M.K.Kelly, O.Ambacher, Appl. Phys. Lett. 69 (12) (1996) and „Fabrication of thin-film InGaN light-emitting diode membranes" W.S.Wrong, T. Sands, Appl. Phys. Lett. 75 (10) (1999)]. This method enables preparation of GaN substrates of a 2-inch diameter.

20   However, their quality is not sufficient for laser diodes, because the dislocation density continues to be approx. 10^7 to approx. $10^9/cm^2$. Recently, the method of lateral epitaxial growth (ELOG) has been used for the reduction of a dislocation density. In this method the GaN layer is first grown on sapphire substrate and then a layer with SiO_2 is deposited on it in the form of strips or lattice. On the thus prepared substrate, in turn, the lateral growth of

25   GaN, leading to a dislocation density lowering to approx. $10^7/cm^2$, may be carried out. The growth of bulk crystals of gallium nitride and other metals of group XIII (IUPAC, 1989) is extremely difficult. Standard methods of crystallization from melt and sublimation methods are not applicable because of the decomposition of the nitrides into metals and N_2. In the HNP method [„Prospects for high-pressure crystal growth of III-V nitrides"

30   S.Porowski *et al.*, Inst. Phys. Conf. Series, 137, 369 (1998)] this decomposition is inhibited

by the use of nitrogen under the high pressure. The growth of crystals is carried out in molten gallium, i.e. in the liquid phase, resulting in the production of GaN platelets about 10 mm in size. Sufficient solubility of nitrogen in gallium requires temperatures of about 1500°C and nitrogen pressures of the order of 15 kbar.

In another known method, the supercritical ammonia was proposed to lower the temperature and decrease the pressure during the growth process. It was shown in particular that it is possible to obtain the crystalline gallium nitride by a synthesis from gallium and ammonia, provided that the latter contains gallium metal amides (KNH_2 or $LiNH_2$). The processes were conducted at temperatures of up to 550°C and under the pressure of 5 kbar, yielding crystals about 5 μm in size [„AMMONO method of BN, AlN, and GaN synthesis and crystal growth" R.Dwiliński et al., Proc. EGW-3, Warsaw, June 22-24, 1998, MRS Internet Journal of Nitride Semiconductor Research, http://nsr.mij.mrs.org/3/25]. Use of a supercritical ammonia also allowed the recrystallization of gallium nitride within the feedstock consisting of a fine-crystalline GaN [„Crystal Growth of gallium nitride in supercritical ammonia" J.W.Kolis et al., J. Cryst. Growth 222, 431-434 (2001)]. The recrystallization was made possible by an introduction of amide (KNH_2) into the supercritical ammonia, along with a small quantity of a halide (KI). Processes conducted at 400°C and 3.4 kbar gave GaN crystals about 0.5 mm in size. However, no chemical transport processes were observed in the supercritical solution, in particular no growth on seeds.

The lifetime of optical semiconductor devices depends primarily on crystalline quality of the optically active layers, and especially on a surface dislocation density. In case of GaN based laser diodes, it is beneficial to lower dislocation density in the GaN substrate layer to less than $10^6/cm^2$, and this is extremely difficult in the methods used so far. Therefore, the main motivation of this invention is to obtain bulk nitride crystals of quality enabling their use as substrates for optoelectronics.

This objective was achieved through developing a process for obtaining of a bulk monocrystalline gallium-containing nitride, which takes place in the autoclave, in the environment of supercritical solvent containing ions of alkali metals, and which comprises dissolving the feedstock and forming a supercritical solution, as well as a crystallization of

a gallium-containing nitride from this solution on the surface of a seed at the temperature higher and/or pressure lower, than that for the dissolution process. The process may comprise the step of feedstock dissolution, and then a separate step of transition of the supercritical solution to higher temperature and/or lower pressure, wherein crystallization

5   of gallium-containing nitride takes place on the surface of a seed. The process may comprise a step of simultaneous creation of at least two zones with different temperatures in the autoclave, whereas the gallium-containing feedstock is placed in the dissolution zone of lower temperature, while the seed is introduced to crystallization zone of higher temperature. The temperature difference between the dissolution zone and crystallization

10   zone is controlled so as to ensure the chemical transport in a supercritical solution, which takes place through convection, and the temperature difference between dissolution zone and crystallization zone is greater than 1°C. The gallium-containing nitride has the form of $Al_xGa_{1-x-y}In_yN$, wherein $0 \leq x < 1$, $0 \leq y < 1$, $0 \leq x+y < 1$ and may contain dopants of donor and/or acceptor and/or magnetic type. The supercritical solvent contains NH_3 and/or its derivatives

15   as well as ions of alkali metals, at least those of potassium. The feedstock consists basically of gallium-containing nitride and/or its precursors selected from a group consisting of azides, imides, amido-imides, amides, hydrides, metallic compounds and gallium-containing alloys, as well as metallic gallium. The seed, on the other hand, contains at least a crystalline layer of a gallium-containing nitride and/or other element(s) of group XIII

20   (according to IUPAC, 1989) of dislocation density below $10^6/cm^2$. The crystallization of a gallium-containing nitride takes place at the temperatures of 100 to 800°C and the pressures between 100 and 10000 bar, while the content of alkali metals ions in supercritical solvent is controlled so as to ensure adequate levels of solubility of both feedstock and gallium-containing nitride, while the molar ratio of alkali metal ions to

25   remaining constituents in supercritical solvent is controlled in the range from 1:200 to 1:2.

The apparatus for obtaining monocrystalline gallium-containing nitride comprises an autoclave for obtaining of a supercritical solvent equipped with an installation for establishing a convection flow, mounted inside a furnace or a set of furnaces equipped with heating and/or cooling devices. The furnace or the set of furnaces has a high-temperature

30   zone coinciding with crystallization zone of the autoclave with heating devices, and a low-

temperature zone coinciding with dissolution zone of the autoclave with heating and/or cooling devices, and may as well have a high-temperature zone with heating and/or cooling devices, as well as a low-temperature zone with heating and/or cooling devices. The installation for establishing convection flow may be made in the form of horizontal baffle or baffles having central and/or circumferential openings, separating the crystallization and dissolution zones. In the autoclave, the feedstock is placed in the dissolution zone and the seed is located in the crystallization zone, while the flow of supercritical solution between dissolution and crystallization zones is determined by the above installation. The dissolution zone is located above the horizontal baffle or horizontal baffles, while the crystallization zone is located below the horizontal baffle or horizontal baffles.

The performed tests showed that the best bulk monocrystalline gallium nitride obtained had the dislocation density close to $10^4/cm^2$ with simultaneous half-width of X-ray rocking curve from (0002) plane below 60 arcsec, providing an appropriate quality and durability of optic semiconductor devices produced with its use.

The object of this invention is illustrated in the Drawing where **Fig. 1** presents the plot of dependence of solubility of GaN in supercritical ammonia that contains potassium amide (with $KNH_2:NH_3=0.07$) on pressure at T=400°C and T=500°C, **Fig. 2** shows the diagram of time variations of temperature in autoclave at p = const for Example 1, **Fig. 3** shows the diagram of time variations of pressure in autoclave at T = const for Example 2, **Fig. 4** presents the diagram of time variations of temperature in autoclave at constant volume for Example 3, **Fig. 5** presents the diagram of time variations of temperature in autoclave for the description of Example 4, **Fig. 6** presents the diagram of time variations of temperature in autoclave for the description of Example 5, **Fig. 7** presents the diagram of time variations of temperature in autoclave for the description of Example 6, **Fig. 8** presents the diagram of time variations of temperature in autoclave for Example 7. In turn **Fig. 9** shows the autoclave, as described in Examples 4, 5, 6, and 7, mounted in furnace set in axial section, and finally the **Fig. 10** is a perspective drawing of the apparatus for obtaining of a bulk monocrystalline gallium-containing nitride.

GaN exhibits good solubility in supercritical NH_3, provided alkali metals or their compounds, such as KNH_2, are introduced into it. Diagram in Fig. 1 presents the GaN

solubility in a supercritical solvent versus pressure for temperatures of 400 and 500°C wherein the solubility is defined by the molar percentage: $S_m \equiv GaN^{solvent} : (KNH_2 + NH_3)$ 100%. In the presented case the solvent is the KNH_2 solution in a supercritical ammonia of a molar ratio $x \equiv KNH_2 : NH_3$ equal to 0.07. The diagram indicates that the solubility is

5 increasing with pressure and decreasing with temperature. These relationships allow to obtain a bulk monocrystalline gallium-containing nitride through its dissolving in the higher solubility conditions, and a crystallization in the lower solubility conditions. In particular, the negative temperature coefficient means that, in the presence of temperature gradient, the chemical transport of gallium-containing nitride shall take place from the

10 dissolution zone of the lower temperature to the crystallization zone of the higher temperature. It also turned out that other gallium compounds, and even metallic gallium, may also be the source of ammonia complexes of gallium. For example, gallium complexes can be introduced to a solvent of the composition specified above from the simplest substrate, such as metallic gallium. Then, through an appropriate modification of

15 conditions (e.g. an increase in temperature) a formation of a supersaturated solution in respect to gallium-containing nitride is achieved and a crystallization on a seed occurs. The process according to invention allows the growth of bulk monocrystalline gallium-containing nitride on the seed and leads in particular to creation of stoichiometric gallium nitride, obtained in the form of monocrystalline bulk layer grown on a gallium-nitride seed.

20 Since such a monocrystal is obtained in a supercritical solution that contains ions of alkali metals, it contains also alkali metals in quantity higher than 0.1 ppm. Because it is desired to maintain a purely basic character of a supercritical solution, mainly in order to avoid corrosion of the apparatus, halides are intentionally not introduced into the solvent. The process enables also to obtain a bulk monocrystalline gallium nitride, wherein from 0.05 to

25 0.5 Ga may be substituted with Al and/or In. The possibility of smooth change of the composition means the possibility of modifying the lattice constant of the nitride obtained. Moreover, the bulk monocrystalline gallium nitride may be doped with dopants of donor (e.g. Si, O) and/or acceptor (e.g. Mg, Zn) and/or magnetic (e.g. Mn, Cr) type in concentrations from 10^{17} to $10^{21}/cm^3$. These dopants modify optical, electric and magnetic

30 properties of a gallium-containing nitride. Concerning the other physical properties, the

bulk monocrystalline gallium nitride has a dislocation density below $10^6/cm^2$, preferably below $10^5/cm^2$, or most preferably below $10^4/cm^2$. Besides, the half-width of its X-ray rocking curve from (0002) plane is below 600 arcsec, preferably below 300 arcsec, and most preferably below 60 arcsec. The best bulk monocrystalline gallium nitride obtained

5   may have dislocation density lower than $10^4/cm^2$ and simultaneously half-width of X-ray rocking curve from (0002) plane below 60 arcsec.

Example 1

   Two crucibles were put into high-pressure autoclave of 10.9 cm³ capacity manufactured according to a known design [H.Jacobs, D.Schmidt, *Current Topics in*

10   *Materials Science,* vol.8, ed. E.Kaldis (North-Holland, Amsterdam, 1981), 381], one of the crucibles containing 0.4 g of the feedstock of gallium nitride in the form of 0.1 mm plates produced by the HVPE method, and the other containing a seed of a double thickness weighing 0.1 g, also obtained by the HVPE method. Further, 0.72 g of metallic potassium of 4N purity was put into the autoclave and the autoclave was filled with 4.81g of ammonia

15   and then closed. The autoclave was put into a furnace and heated to the temperature of 400°C. The pressure within the autoclave was 2 kbar. After 8 days the temperature was increased to 500°C, while the pressure was maintained at the 2 kbar level and the autoclave was maintained in these conditions for another 8 days (the diagram in Fig. 2). As a result of the process the feedstock became completely dissolved and the recrystallization of gallium

20   nitride layer took place on the partially dissolved seed.

Example 2

   Two crucibles were put into high-pressure autoclave of 10.9 cm³, one of the crucibles containing 0.44 g of the feedstock of gallium nitride in the form of 0.1mm thick plates produced by the HVPE method, and the other containing a seed of a double

25   thickness weighing 0.1g, also obtained by the HVPE method. Further, 0.82 g of metallic potassium of 4N purity was put into the autoclave and the autoclave was filled with 5.43g of ammonia and then closed. The autoclave was put into a furnace and heated to temperature of 500°C. The pressure within the autoclave was 3.5 kbar. After 2 days the pressure was lowered to 2 kbar, while the temperature was maintained at the 500°C level

and the autoclave was maintained in these conditions for another 4 days (the diagram in Fig. 3). As a result of the process the feedstock became completely dissolved and the recrystallization of gallium nitride layer took place on the partially dissolved seed.

Example 3

Two crucibles were put into high-pressure autoclave of 10.9 cm^3, one of the crucibles containing 0.3 g of the feedstock in the form of metallic gallium of 6N purity and the other containing a 0.1g seed obtained by the HVPE method. Further, 0.6 g of metallic potassium of 4N purity was put into the autoclave and the autoclave was filled with 4 g of ammonia and then closed. The autoclave was put into a furnace and heated to temperature of 200°C. After 2 days the temperature was increased to 500°C, while the pressure was maintained at the 2 kbar level and the autoclave was maintained in these conditions for further 4 days (the diagram in Fig. 4). As a result of the process the feedstock became completely dissolved and the recrystallization of gallium nitride layer took place on the seed.

Example 4

The amount of 3.0g of gallium nitride produced by the HVPE method was put into high-pressure autoclave 1 of 35.6 cm^3 capacity (Fig. 9). This amount was distributed in equal portions in the dissolution zone 13 and the crystallization zone 14. Metallic potassium of 4N purity was also added in quantity of 2.4g. Then the autoclave 1 was filled with 15.9g of ammonia (5N), closed, put into a set of furnaces 4 and heated to temperature of 450°C. The pressure inside the autoclave 1 was approx. 2 kbar. After an entire day the temperature of the crystallization zone 14 was increased to 500°C while the temperature of the dissolution zone 13 was lowered to 400°C and the autoclave 1 was kept in these conditions for the subsequent 6 days (the diagram in Fig. 5). As a result of this process the partial dissolution of material in the dissolution zone 13 and the growth of gallium nitride on gallium-nitride seeds in the crystallization zone 14 took place.

Example 5

A high pressure autoclave 1 of 35.6 cm^3 capacity (Fig. 9) is charged with the feedstock in the form of 3.0g pellet of sintered gallium nitride (introduced into the

dissolution zone 13), seeds of gallium nitride obtained by the HVPE method (introduced into the crystallization zone 14), as well as with 2.4g of metallic potassium of 4N purity. Then the autoclave was filled with 15.9g of ammonia (5N) and closed. The autoclave 1 was then put into a set of furnaces 4 and heated to 480°C. The pressure inside the autoclave was about 2 kbar. After an entire day the temperature of the crystallization zone 14 was raised to 500°C, while the temperature of dissolution zone 13 was lowered to 420°C and the autoclave was maintained in this conditions for further 6 days (the diagram in Fig. 6). As a result of the process the feedstock became partially dissolved in the dissolution zone 13 and gallium nitride grew on seeds in the crystallization zone 14.

Example 6

A high pressure autoclave 1 of 36 cm³ capacity (Fig. 9) was charged with 1.6g of the feedstock in the form of gallium nitride produced with the HVPE method (introduced into the dissolution zone 13), 0.8g of gallium nitride seeds, also obtained by the HVPE method (introduced into the crystallization zone 14), as well as with 3.56 g of metallic potassium of 4N purity. The autoclave 1 was filled with 14.5g of ammonia (5N) and closed. Then the autoclave 1 was put into a set of furnaces 4 and heated to 425°C. The pressure inside the autoclave was approx. 1.5 kbar. After an entire day the temperature of dissolution zone 13 was lowered to 400°C while the temperature of crystallization zone 14 was increased to 450°C and the autoclave was kept in these conditions for the subsequent 8 days (the diagram in Fig. 7). After the process the feedstock was found to be partially dissolved in dissolution zone 13 and gallium nitride grew on seeds of the HVPE GaN in the crystallization zone 14.

Example 7

A high pressure autoclave 1 of 36 cm³ capacity (Fig. 9) was charged in its dissolution zone 13 with 2g of a feedstock in the form of gallium nitride produced by the HVPE method and 0.47g of metallic potassium of 4N purity and in its crystallization zone 14 with 0.7g of GaN seeds also obtained by the HVPE method. The autoclave was filled with 16.5g of ammonia (5N) and closed. Then the autoclave 1 was put into a set of furnaces 4 and heated to 500°C. The pressure inside the autoclave was approx. 3 kbar.

After an entire day the temperature in the dissolution zone <u>13</u> was reduced to 450°C while the temperature in the crystallization zone <u>14</u> was raised to 550°C and the autoclave was kept in these conditions for the following 8 days (the diagram in Fig. 8). After the process the feedstock was found to be partially dissolved in the dissolution zone <u>13</u> and gallium nitride grew on seeds in the crystallization zone <u>14</u>.

The described process is carried out in the apparatus for obtaining bulk mono-crystalline gallium-containing nitride in a supercritical solvent. The basic unit of the apparatus is the autoclave <u>1</u> for obtaining solvent in a supercritical state, equipped with an installation <u>2</u> for providing a chemical transport of a solvent in a supercritical solution inside the autoclave <u>1</u>. For this purpose, the autoclave <u>1</u> is put into a chamber <u>3</u> of a set of two furnaces <u>4</u> provided with heating <u>5</u> and/or cooling <u>6</u> devices and secured in a desired position in respect to furnaces <u>3</u> by means of screw-type blocking device <u>7</u>. The furnaces <u>4</u> are mounted on a bed <u>8</u> and secured by means of steel tapes <u>9</u> wrapped around the furnaces <u>4</u> and the bed <u>8</u>, and the bed, together with the set of furnaces <u>4</u> is mounted rotationally in base <u>10</u> and secured in desired angular position by means of pin interlock <u>11</u>. Due to this the speed and type of convection flow in autoclave <u>1</u> can be controlled. In the autoclave <u>1</u>, placed in the set of furnaces <u>4</u>, the convection flow of supercritical solution takes place as determined by the installation <u>2</u>, made in the form of horizontal baffle or horizontal baffles <u>12</u> with central and/or circumferential opening, separating the dissolution zone <u>13</u> from the crystallization zone <u>14</u> in the autoclave <u>1</u>, while the temperature level of individual zones in the autoclave <u>1</u> in the temperature range from 100 to 800°C is set on furnaces <u>4</u> by means of a control system <u>15</u>. In the autoclave <u>1</u>, the dissolution zone <u>13</u> coinciding with the low-temperature zone of the set of furnace <u>4</u>, is located above the horizontal baffle or horizontal baffles <u>12</u> and the feedstock <u>16</u> is put into said zone <u>13</u>. On the other hand, the crystallization zone <u>14</u> coincides with the high-temperature zone of the set of furnace <u>4</u> and it is located below the horizontal baffle or baffles <u>12</u>. The seed <u>17</u> is mounted in this zone while the mounting location of said seed <u>17</u> is set below the intersection of rising and descending convection streams.

Due to a good crystalline quality the obtained bulk monocrystalline gallium-containing nitride may be used as a substrate material for optoelectronic semiconductor devices based on nitrides, in particular for laser diodes.

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PATENT ATTORNEY
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Record number 1456

Claims

1.   A process for obtaining a bulk monocrystalline gallium-containing nitride, characterized in that it is performed in an autoclave, in the environment of a supercritical solvent containing ions of alkali metals, wherein the feedstock becomes dissolved to form supercritical solution, and the gallium-containing nitride becomes crystallized from that solution on the surface of a seed at the temperature higher and/or pressure lower than the temperature of the dissolution.

2.   The process according to claim 1, characterized in that said process comprises the steps of dissolving the feedstock and a separate step of transferring the supercritical solution to the higher temperature and/or to the lower pressure.

3.   The process according to claim 1, characterized in that said process comprises the step of simultaneous creation of at least two zones of different temperatures, said gallium-containing feedstock is placed in the dissolution zone of the lower temperature, while the seed is placed in the crystallization zone of the higher temperature.

4.   The process according to claim 3, characterized in that said temperature difference between said dissolution zone and said crystallization zone is controlled as to ensure chemical transport in the supercritical solution.

5.   The process according to claim 4, characterized in that said chemical transport in the supercritical solution takes place through convection.

6.   The process according to claim 4, characterized in that said temperature difference between the dissolution zone and the crystallization zone is greater than $1^{\circ}C$.

7.   The process according to claim 1, characterized in that said gallium-containing nitride has the form of $Al_xGa_{1-x-y}In_yN$, where $0 \leq x < 1$, $0 \leq y < 1$, $0 \leq x+y < 1$.

8.   The process according to claim 1, characterized in that said gallium-containing nitride may contain dopants of a donor and/or acceptor and/or magnetic type.

9.   The process according to claim 1, characterized in that said supercritical solvent contains NH_3 and/or its derivatives.

10.   The process according to claim 1, characterized in that said supercritical solvent contains at least potassium ions.

11.   The process according to claim 1, characterized in that said feedstock consists basically of a gallium-containing nitride and/or its precursors.

12.   The process according to claim 11, characterized in that said precursors are selected from a group consisting of azides, imides, amido-imides, amides, hydrides, metallic compounds and gallium-containing alloys, as well as metallic gallium.

13.   The process according to claim 1, characterized in that said seed has at least a crystalline layer of a gallium-containing nitride and/or other elements of Group XIII (according to IUPAC, 1989).

14.   The process according to claim 1, characterized in that said seed has at least a crystalline layer of gallium-containing nitride with a dislocation density below $10^6/cm^2$.

15.   The process according to claim 1, characterized in that said crystallization of a gallium-containing nitride takes place at the temperatures from 100 to 800°C.

16.   The process according to claim 1, characterized in that said crystallization of a gallium-containing nitride takes place at the pressures from 100 to 10000 bar.

17.   The process according to claim 1, characterized in that the content of alkali metal ions in a supercritical solvent is controlled so as to provide adequate levels of solubility of said feedstock as well as said gallium-containing nitride.

18.   The process according to claim 1, characterized in that the molar ratio of said alkali-metal ions to the remaining components in a supercritical solvent is controlled within the range of 1:200 to 1:2.

19.   An apparatus for obtaining of a monocrystalline gallium-containing nitride, comprising autoclave (1) for producing of supercritical solvent, equipped with installation (2) for establishing a convection flow, mounted inside furnace or set of furnaces (4) equipped with heating (5) and/or cooling (6) devices.

20. The apparatus according to claim 19, characterized in that said furnace or set of furnaces (4) has the high-temperature zone coinciding with the crystallization zone (14) of said autoclave (1) equipped with heating devices (5), and the low-temperature zone coinciding with dissolution zone (13) of the autoclave (1) equipped with heating (5) and/or cooling (6) devices.

21. The apparatus according to claim 19, characterized in that said furnace or set of furnaces (4) has the high-temperature zone coinciding with the crystallization zone (14) of said autoclave (1) equipped with heating (5) and/or cooling (6) devices, as well as the low-temperature zone coinciding with the dissolution zone (13) of the autoclave (1) equipped with heating (5) and/or cooling (6) devices.

22. The apparatus according to claim 19, characterized in that said installation (2) is made in the form of a horizontal baffle or horizontal baffles (12) having central and/or circumferential openings, separating the crystallization zone (14) from the dissolution zone (13).

23. The apparatus according to claim 19, characterized in that said feedstock (16) is placed in autoclave (1) in the dissolution zone (13), and said seed (17) is placed in the crystallization zone (14), and said flow of supercritical solution between the zones (13) and (14) is established by said installation (2).

24. The apparatus according to claim 22, characterized in that said dissolution zone (13) is located above said horizontal baffle or horizontal baffles (12), whereas said crystallization zone (14) is located below said horizontal baffle or horizontal baffles (12).
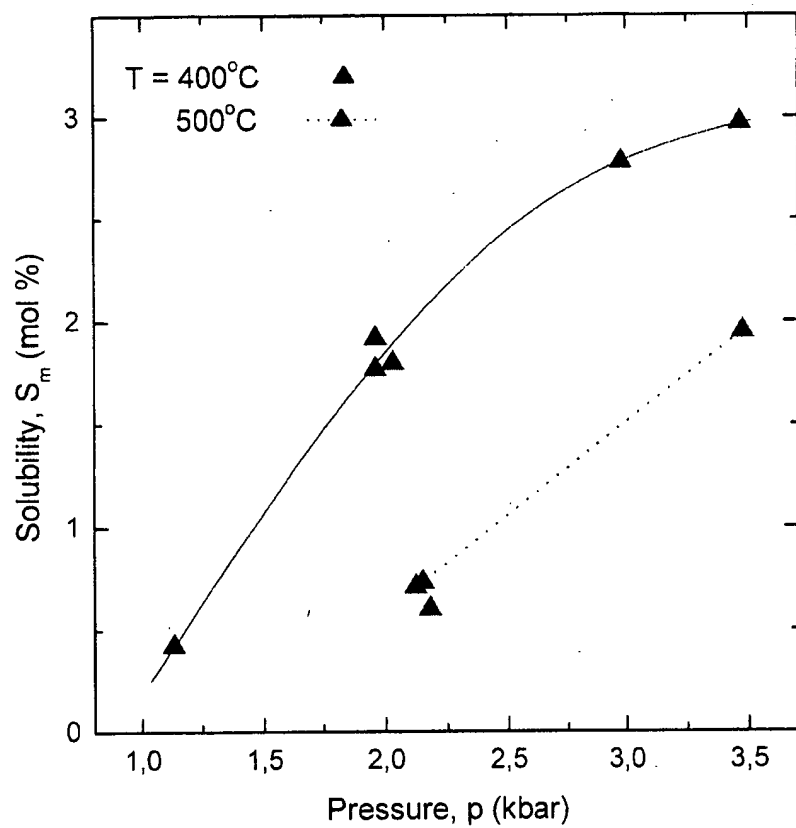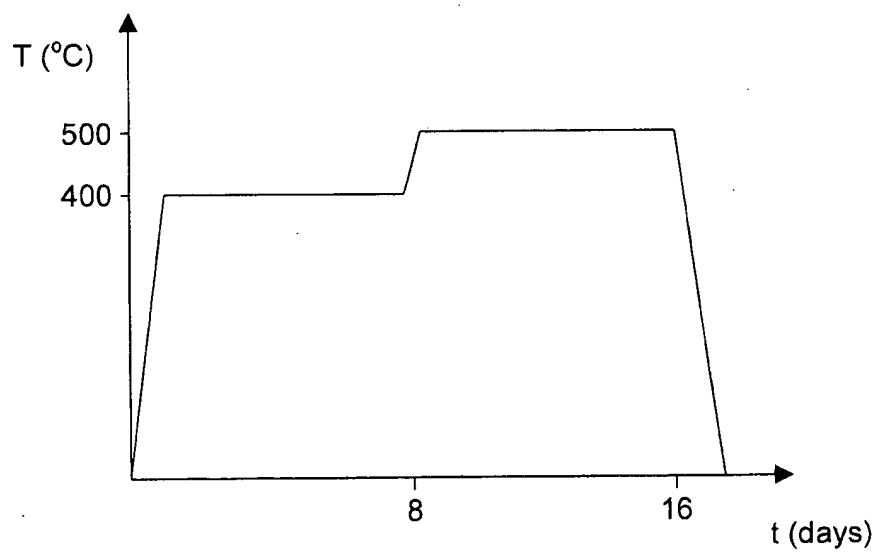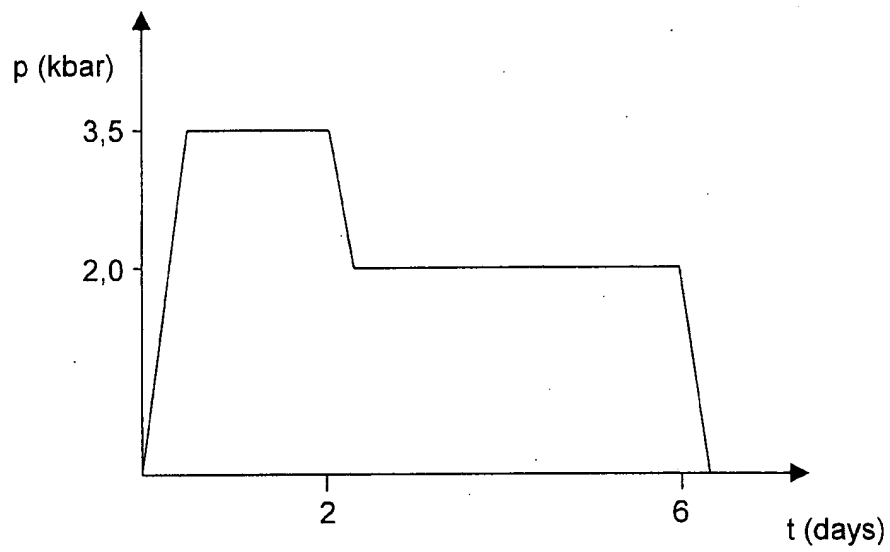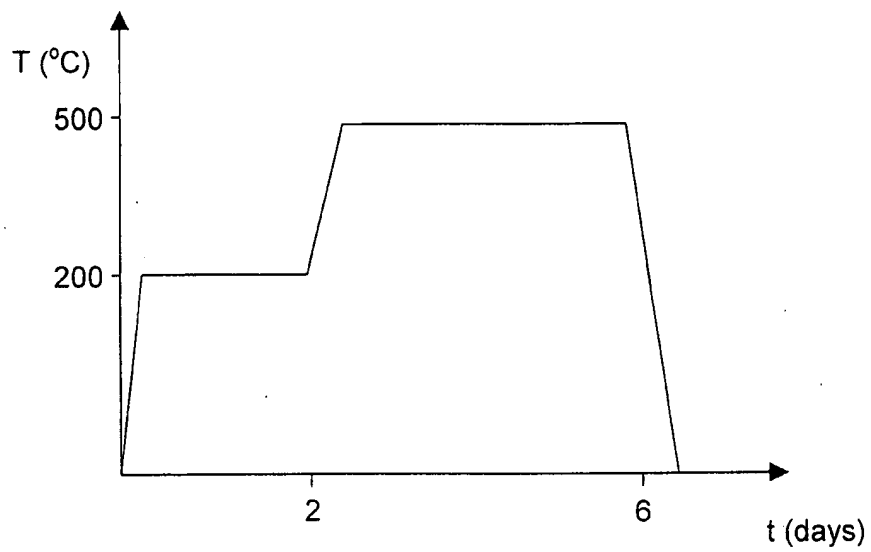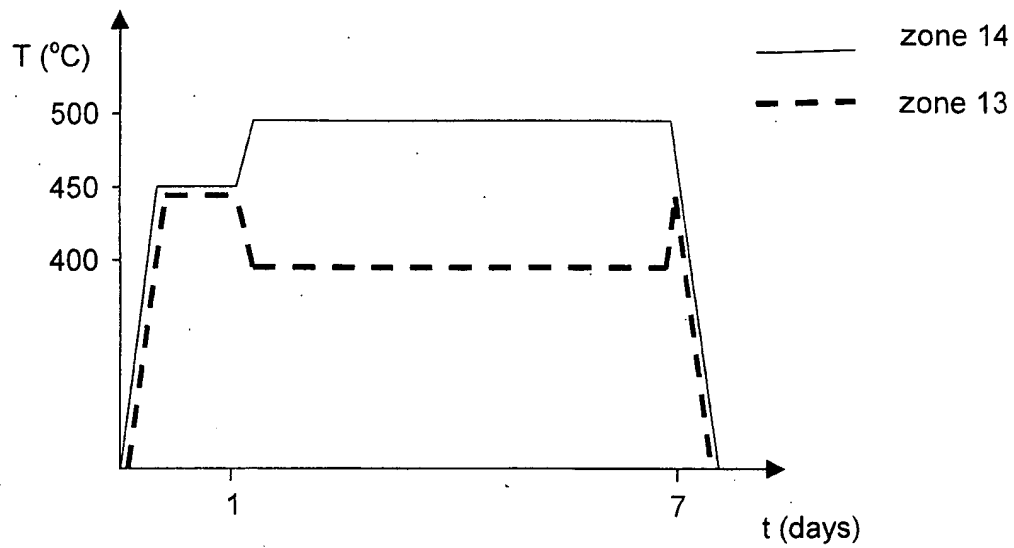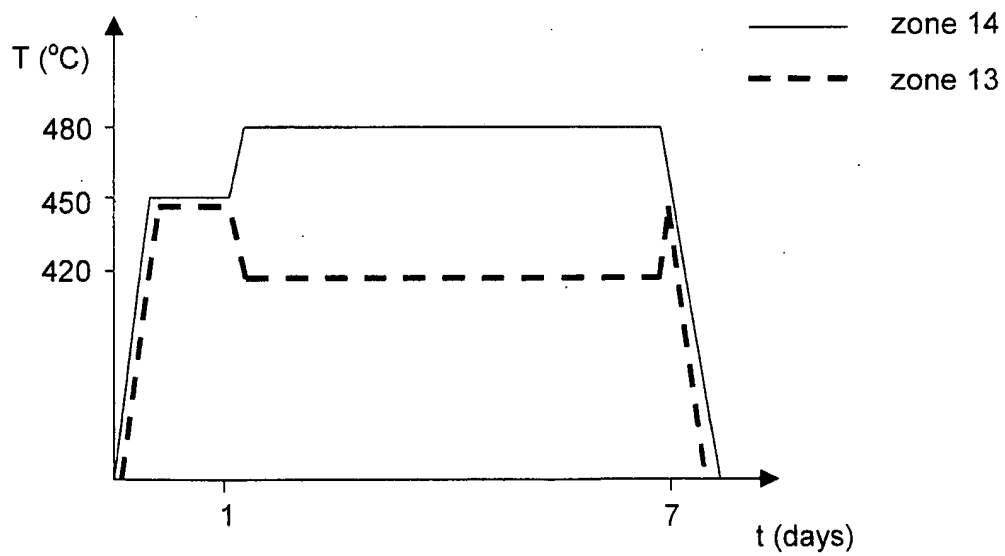
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7
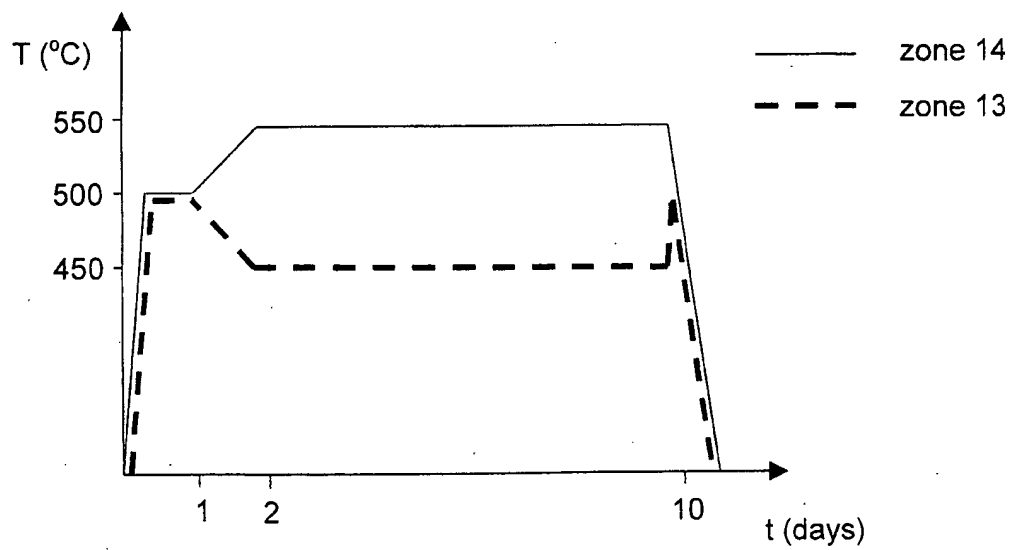

Fig. 8

Fig. 9

1   4   9   11   10   15   4   8

3

7

Fig. 10